Generation of 9-Stannaphenanthrene and Its Reactivities

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(Received April 15, 2005; CL-050520)

A neutral stannaaromatic compound, 9-stannaphenanthrene **1a** bearing an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt), was successfully generated by the reaction of the corresponding chlorostannane **2** with lithium 2,2,6,6-tetramethylpiperidide in THF at $-78\,^{\circ}\mathrm{C}$. The generaion of **1a** was indicated by the trapping experiments using MeOD, Mes*CNO, and 2,3-dimethyl-1,3-butadiene at the same temperature. However, **1a** was found to undergo ready dimerization at room temperature to give the *cis*-[2 + 2] dimer **3** stereoselectively.

In recent years, much attention has been focused on stannaaromatic compounds, i.e., Sn-containing $[4n+2]\pi$ electron ring systems. In view of the recent progress in the chemistry of sila- and germaaromatic compounds, the synthesis of stannaaromatic compounds is of great interest from the standpoint of systematic elucidation of heavier congeners of aromatic hydrocarbons,[1] which play very important roles in organic chemistry. Although stannole dianions[2] have been successfully synthesized as stable compounds and fully characterized as ionic stannaaromatic compounds, neutral stannaaromatic compounds are still elusive and their properties have not been disclosed yet so far. The main reason for the lack of neutral stannaaromatic compounds is due to the difficulty in their synthesis and isolation responsible for the extremely high reactivity of tin–carbon double bonds.[3] On the other hand, we have recently succeeded in the synthesis and isolation of kinetically stabilized, neutral sila- and germaaromatic compounds[4,5] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl (Tbt). With these stable systems in hand, we have revealed their molecular structures and reactivities and have discussed the aromaticity of sila- and germaaromatic compounds. The successful results in the sila- and germaaromatic systems naturally prompted us to extend this chemistry to the heavier metallaaromatic systems of group 14 elements. Here, we report the generation of 9-stannaphenanthrene **1a** kinetically stabilized by the Tbt group, the first neutral stannaaromatic compound (Figure 1).

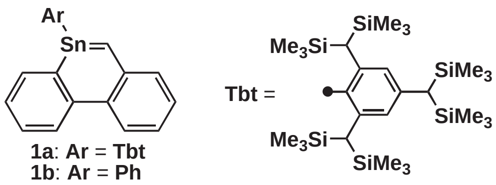
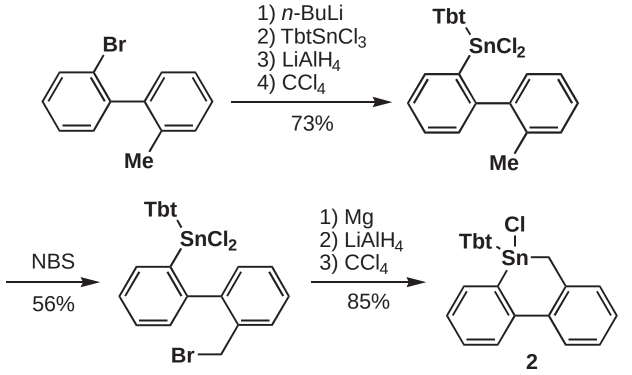


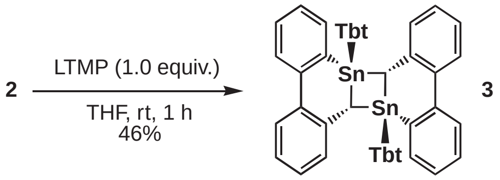
Figure 1.

9-Chloro-9,10-dihydro-9-stannaphenanthrene **2**,[6] the suitable precursor of **1a**, was prepared according to Scheme 1. Since a considerable amount of bromostannanes were formed in the first (stannylation) and third (reductive cyclization) steps due to the ready halogen-exchange reactions with LiBr and MgBrCl, respectively, the initially generated halostannanes were subjected to the $\mathrm{LiAlH_4}$ reduction followed by the rechlorination with $\mathrm{CCl_4}$ in both steps with the intension of transforming into the corresponding pure chlorostannanes.



Scheme 1.

Synthesis of **1a** was first attempted by the dehydrochlorination of **2** with various kinds of bases [lithium diisopropyl amide (LDA), lithium hexamethyldisilazide (LHMDS), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and *tert*-butyl lithium].[6] Although no evidence for the generation of **1a** was obtained in these cases, the reaction of **2** with lithium 2,2,6,6-tetramethylpiperidide (LTMP) at room temperature resulted in the stereoselective formation of *cis*-[2 + 2] dimer **3**[6] (46%) of 9-stannaphenanthrene **1a** (Scheme 2). The molecular structure of **3** was unambiguously determined by X-ray crystallographic analysis (Figure 2).[7]



Scheme 2.

Since the formation of **3** suggested the generation of **1a** as a transient species, the trapping experiments at low temperature were examined. To the reaction mixture of **2** and LTMP were added MeOD, Mes*CNO [Mes* = 2,4,6-tri(*tert*-butyl)phenyl], and 2,3-dimethyl-1,3-butadiene as trapping reagents at $-78\,^{\circ}\mathrm{C}$ to give the corresponding adducts **4a** (almost quantitative as estimated by ^{1}H NMR), **5** (43% isolated yield), and **6** (67% isolated yield), respectively (Scheme 3). Compound **4a** was moisture-sensitive and could not be isolated as a pure compound because of the difficulty in the separation from 2,2,6,6-tetramethylpiperidine, which is the inevitable by-product of this reaction. The molecular structure of **4a** was determined by the comparison with pure **4b**[6] which was prepared by the reaction

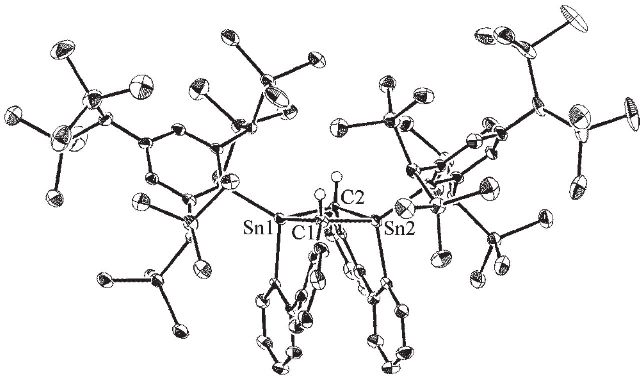
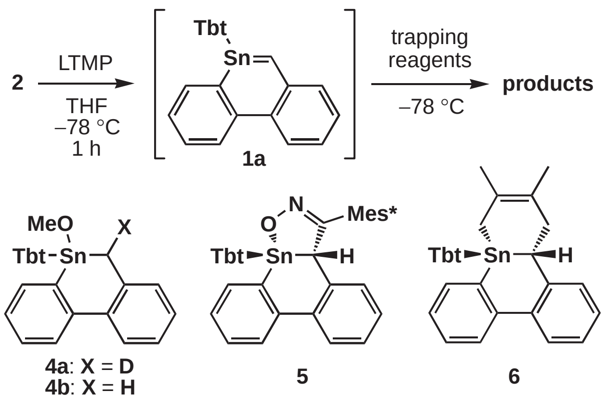


Figure 2. ORTEP drawing (50% probability) of **3**.

of **2** with LiOMe in THF. The molecular structures of **5** and **6** were confirmed with the ^{1}H, ^{13}C, and ^{119}Sn NMR and mass spectral data,[6] and were finally established by X-ray crystallographic analysis (Figure 3).[8] Since 2,3-dimethyl-1,3-butadiene is inert to anionic species such as 9-chloro-10-lithio-9-Tbt-9,10-dihydro-9-stannaphenanthrene, which is an alternative intermediate in the reactions of **2** with LTMP giving **3**, **4a**, and **5**, the formation of a [2 + 4] cycloadduct **6** from **2** indicates that the reaction of **2** with LTMP affords not an anionic intermediate but a neutral stannaphenanthrene **1a**. These results strongly indicate that **1a** exists as a monomer in a THF solution at −78 °C.[9] The thermal instability of **1a** is in sharp contrast to the high stability of Tbt-substituted 9-silaphenanthrene (**7**),[10] which is stable at 100 °C in C_6D_6. In theoretical calculations using a Ph-substituted model **1b**,[11] it was found that the planar conformation of the 9-stannaphenanthrene skeleton is not a local minimum, that is, the 9-stannaphenanthrene ring of **1b** consists of a localized Sn=C unit and a biphenyl unit in contrast to the 9-silaphenanthrene ring of **7**, the X-ray crystallographic analysis of which has revealed its planar and π-electron-delocalized structure.[10] The thermal instability of **1a** and the theoretical calculations suggest the small contribution of aromatic stabilization in the 9-stannaphenanthrene system of **1a**.



Scheme 3.

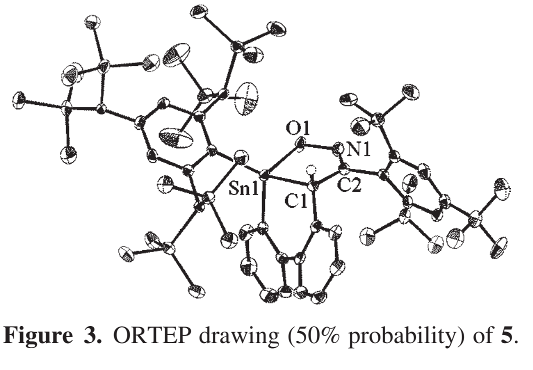


Figure 3. ORTEP drawing (50% probability) of **5**.

In summary, we have succeeded in the generation of 9-stannaphenanthrene **1a** for the first time and revealed its high reactivities. With the hope of isolating **1a** as a stable compound, further investigation on the introduction of additional substituent(s) to the stannaphenanthrene skeleton and the cooperative stabilization method (the contribution of kinetic and thermodynamic stabilization) are currently in progress.

This work was supported by Grants-in-Aid for COE Research on Elements Science (No. 12CE2005), Scientific Research on Priority Area (No. 14078213), Scientific Research (A) (No. 14204064) and the 21st Century COE Program on Kyoto University Alliance for Chemistry from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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6 Experimental procedures and physical properties for the precursor **2** and the products **3**, **4b**, **5**, and **6** are described in the Supporting Information.

7 Crystal data for **3**: $C_{80}H_{136}Si_{12}Sn_2\cdot C_6H_6$ MW = 1750.46; triclinic; space group $P\bar{1}$; $a = 12.8898(2)$ Å, $b = 17.9414(3)$ Å, $c = 22.3902(5)$ Å; $\alpha = 81.1212(8)°$, $\beta = 82.9007(9)°$, $\gamma = 72.8807(16)°$; $V = 4872.49(16)$ Å^3; $Z = 2$; $D_{calcd} = 1.193$ g/cm^3; $\mu = 0.699$ mm^{-1}; $2\theta_{max} = 50°$; $T = 103$ K; $R_1(I > 2\sigma(I)) = 0.0451$; wR_2 (all data) = 0.1015; GOF = 1.020 for 16862 reflections and 937 parameters, (CCDC 268569).

8 Crystal data for **5**: $C_{59}H_{97}NOSi_6Sn$ MW = 1123.61; triclinic; space group $P\bar{1}$; $a = 9.8361(9)$ Å, $b = 15.5831(11)$ Å, $c = 21.8919(17)$ Å; $\alpha = 107.957(3)°$, $\beta = 96.281(3)°$, $\gamma = 88.936(7)°$; $V = 3172.5(4)$ Å^3; $Z = 2$; $D_{calcd} = 1.176$ g/cm^3; $\mu = 0.552$ mm^{-1}; $2\theta_{max} = 50°$; $T = 103$ K; $R_1(I > 2\sigma(I)) = 0.0309$; wR_2 (all data) = 0.0907; GOF = 1.014 for 10703 reflections and 716 parameters, (CCDC 268570). Crystal data for **6** is described in the Supporting Information.

9 Additional information: 1) When these trapping experiments were performed after stirring for 1 h at −40 °C, dimer **3** was obtained in ca. 30% yield. 2) Dimer **3** showed no change in C_7D_8 at 100 °C and did not react with Mes*CNO in C_6D_6 even at 80 °C, indicating no dissociation of **3** to the monomer **1a** in solution.

10 A. Shinohara, N. Takeda, T. Sasamori, and N. Tokitoh, The 7th IUPAC International Conference on Heteroatom Chemistry, Shanghai, China, August 2004, Abstr., No. P43.

11 Theoretical calculations were carried out using the Gaussian 98 program with density functional theory at the B3LYP level. In calculations, LANL2DZ (for Sn) and 6-31G(d) (for C and H) basis sets were used. The optimized structure of **1b** is shown in the Supporting Information.

Published on the web (Advance View) July 2, 2005; DOI 10.1246/cl.2005.1088